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The synthesis, characterization and polycondensation of metal-containing diols: crystal structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2)_3O\text{-}\{2,6\text{-}(CH_2OH)_2\text{-}4\text{-}CH_3-C_6H_2\}]$

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The synthesis of two new transition-metal-containing polyesters is described. The precursors are bifunctional organometallic monomers that were synthesized using 2,6-bis(hydroxymethyl)-*p*-cresol as the key reagent. This was achieved by simple coupling reactions between the appropriate organometallic alkyl halide and the cresol reagent. Polycondensation reactions were carried out with terephthaloyl chloride using ambient temperature solution techniques. The new low molecular weight oligomeric polyesters were characterized using Fourier transform infrared and ^{1}HNMR spectroscopy, differential scanning calorimetry, thermogravimetric analysis and size-exclusion chromatography analyses. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: metal-containing diols; organometallic polymers; polyesters; 2,6-bis(hydroxymethyl)-*p*-cresol; metallopolyesters

INTRODUCTION

Organometallic polymer[1] chemistry is a prolific area of research, which has been underscored by the synthesis of new products with special chemical and physical properties.[2,3] These new materials are regarded as having promising applications in areas such as non-linear optics[4,5] and catalysis.[6–9] Condensation organometallic polymers, in particular, have received little attention. Polycondensation of organometallic monomers represents a field of organometallic polymer chemistry, where organometallic monomers bearing suitable bifunctional moieties, can undergo classical organic or inorganic condensation polymerization reactions. These types of polymers include a range of materials where the organometallic moiety is either pendant to the polymer backbone[10–12] or is in the main chain.[13–16] Novel ways of introducing bifunctional moieties into organometallic complexes have been developed, and a number of examples can be found in the literature. Recently, Masuda and co-workers[17,18] prepared Fischer-type organometallic bifunctional alkoxycarbene complexes and reacted these with diamines, to form organometallic polymers containing metals in the main polymer chain. Abd-El-Aziz *et al.*[12] synthesized organometallic polyethers, thioethers and amines with the metal moieties pendant to the polymer backbone. Their strategies involved reacting cyclopentadienyliron complexes of dichloroarenes with various oxygen and sulfur dinucleophiles. There are few reports on organometallic polyesters, the earliest extensive work being carried out by the Pittman group.[19,20] More recently, Endo and co-workers[21] reported the synthesis of cobaltacyclopentadiene derivatives bearing bifunctional hydroxy functionalities. Polycondensation reactions of these organocobalt bisphenols with a range of alcohols and acid chlorides gave rise to a host of polyethers and polyesters respectively.[21]

Synthetic routes for preparing bifunctional organometallic monomers are often not straightforward, and they vary from compound to compound. There is thus a need for the construction of new organometallic monomers and perhaps the modification of existing systems. In this paper we report on the preparation of some new organometallic polyesters.

First, the synthesis and characterization of new organometallic monomers (Fig. 1) that contain polymerizable bifunctional groups is described. Our research efforts have focused on using 2,6-bis(hydroxymethyl)-*p*-cresol as the key reagent to prepare some new transition-metal-containing bifunctional monomers, for further polycondensation reac-

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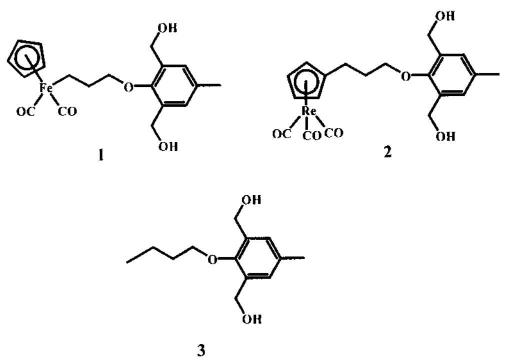


Figure 1. New bifunctional monomers.

tions. The syntheses of these monomers were based on the organic coupling reactions employed by Fréchet and coworkers.[22,23] Second, polycondensation reactions were carried out in solution at room temperature to produce new organometallic polyesters.

EXPERIMENTAL

General

All reactions were carried out under nitrogen using standard Schlenk tube techniques, unless otherwise stated. Tetrahydrofuran (THF) and toluene were dried over sodium–benzophenone and distilled under nitrogen before use. Acetone was dried and distilled over $CaCl_2$. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 1,3-dibromopropane, 2,6-bis(hydroxymethyl)-*p*-cresol and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) were purchased from Sigma–Aldrich. Potassium carbonate, terephthaloyl chloride and triethylamine were obtained from SAARCHEM. $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2)_3Br]$[24] and $[\{\eta^5\text{-}(C_5H_4)CH_2CH_2CH_2I\}Re(CO)_3]$[25] were prepared according to literature procedures. All column chromatography was done on either deactivated alumina 90 (70–230 mesh) or silica gel (70–230 mesh), obtained from Merck. Infrared spectra were recorded on a Perkin Elmer Paragon 1000PC FT-IR spectrophotometer, using either solution cells with NaCl windows or diffuse reflectance infrared transmission spectroscopy (DRIFTS) in a KBr matrix. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Mass spectra were obtained with a V.G. Micromass 16F spectrometer, operating at 70 eV ionizing voltage. Melting points were determined on a Fischer–Johns hot-stage microscope, and are uncorrected. Gel permeation chromatography (GPC) analysis of the molecular weight distribution of the polymers was performed on a system equipped with a Spectra Physics RI detector, a Spectra Physics LC pump, and Spectra Physics Winner software. A series of four 300 mm × 7.8 mm columns was packed with 10 μm packing material of phenogel (styrene–divinylbenzene). These had pore sizes of 100, 500, 10^3, and 10^4 Å. The eluting solvent was THF at a flow rate of 1.25 ml/ min. The system was calibrated against polystyrene standards: M_p 580, 1320, 5050, 7000, 11 600, 66 000 and 156 000. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) data were performed at the University of Cape Town on a Perkin–Elmer PC7 Series Thermal Analysis System, at a scanning rate of 10 °C/ min^{-1} under nitrogen gas-purge with a flow rate of 30 ml/ min^{-1}.

X-ray intensity data were collected at 173 K on a Nonius Kappa CCD with 1.5 kW graphite monochromated Molybdenum radiation. The strategy for the data collection was evaluated using the COLLECT software.[26] The data were scaled and reduced using DENZO-SMN.[27] Unit-cell dimensions were refined on all data. The structure was solved and refined using SHELX97.[28] Hydrogen atoms belonging to Cp-ring and methyl carbons were placed in calculated positions. All other hydrogen atoms were located from difference electron density maps. The plot of the molecular structure for publication was obtained using the program PLATON.[29]

Preparation of monomer 1

2,6-Bis(hydroxymethyl)-*p*-cresol (0.566 g, 3.36 mmol), K_2CO_3 (1.40 g, 10.1 mmol) and 18-crown-6 (0.179 g, 0.677 mmol) were transferred to a nitrogen-purged Schlenk tube and taken up in freshly distilled acetone (10 ml), to give a dark orange–brown slurry. $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2)_3Br]$ (1.01 g, 3.36 mmol) was dissolved in freshly distilled acetone (10 ml) and added dropwise to the stirred slurry. This mixture was heated to reflux and stirred vigorously for 48 h. The reaction mixture was cooled to room temperature, the solvent removed using a rotary evaporator and the resulting oily residue extracted with CH_2Cl_2. After filtration by gravity and removal of the solvent, the residual oil was transferred to an alumina column, using hexane as eluent. The desired major product was contained in the second fraction that was eluted with a 70% CH_2Cl_2–hexane mixture. Removal of the solvent gave a light-brown solid, in 39% yield.

^1H NMR (200 MHz, $CDCl_3$, δ): 1.46 (t, 2H, $FeCH_2$), 1.93 (m, 2H, CH_2), 2.31 (s, 3H, CH_3), 3.80 (t, 2H, CH_2OAr), 4.70 (s, 4H, CH_2OH), 4.78 (s, 5H, Cp), 7.12 (s, 2H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 2.86 ($FeCH_2$), 20.74 (CH_2), 38.34 (CH_3), 61.31 (CH_2OAr), 85.42 (Cp), 77.97 (CH_2OH), 129.40, 133.80, 134.07, 153.20 (Ar), 217.48 (CO). IR (CH_2Cl_2), ν(CO) cm^{-1}: 2005 (s), 1945 (s). M.p.: 102–103 °C.

Anal. Found C, 59.04; H, 5.70. Calc. for $C_{19}H_{22}FeO_5$: C, 59.10; H, 5.70%. Mass spectra (*m/z*): 330 [53%, $(\eta^5\text{-}C_5H_5)Fe(CH_2)_3O\text{-}\{2,6\text{-}(CH_2OH)_2\text{-}4\text{-}CH_3{-}C_6H_2\}$], 205 [84%, $(\eta^5\text{-}C_5H_5)(CO)_2Fe(CH_2CH_2{-})$], 121 [100%, $(\eta^5\text{-}C_5H_5)Fe$].

Preparation of monomer 2

A Schlenk tube was evacuated and filled with nitrogen. 2,6-Bis(hydroxymethyl)-*p*-cresol (0.215 g, 1.28 mmol), K_2CO_3 (0.270 g, 1.95 mmol) and 18-crown-6 (0.0540 g, 0.204 mmol) were transferred to the Schlenk tube, together with [η^5-(C_5H_4)$CH_2CH_2CH_2I$]$Re(CO)_3$ (0.650 g, 1.27 mmol) and freshly distilled acetone (20 ml). The reaction mixture was refluxed for 48 h under a nitrogen atmosphere. The solvent was then removed under reduced pressure, and the resulting residue dissolved in CH_2Cl_2. After filtration by gravity, the solution was concentrated using a rotary evaporator, and transferred to a silica gel column. Purification was achieved by column chromatography, using a column made up with 5% ethylacetate (in CH_2Cl_2). The polarity was slowly increased to 10% ethylacetate–CH_2Cl_2, to elute the desired product. The product was isolated as a white solid in 85% yield.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 1.98 (m, 2H, CH_2), 2.31 (s, 3H, CH_3), 2.67 (t, 2H, $-CH_2Cp$), 3.88 (t, 2H, $-CH_2O-$), 4.65 (s, 4H, CH_2OH), 5.24–5.29 (m, 4H, Cp), 7.13 (s, 2H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 20.78 ($-CH_2-$), 24.71 ($-CH_2Cp$), 32.27 (CH_3), 60.85 ($-CH_2OAr$), 74.02 (CH_2OH), 83.08, 83.67 (Cp), 129.56, 133.58, 134.31, 152.67 (Ar), 194.38 (CO). IR (CH_2Cl_2), ν(CO) cm^{-1}: 2020 (s), 1923 (s). M.p.: 98–99 °C.

Anal. Found: C, 43.35; H, 4.16. Calc. for $C_{20}H_{21}O_6Re$: C, 44.19; H, 3.89%. Mass spectra (*m/z*): 544 [52%, molecular ion peak], 460 [6%, Re(η^5-$C_5H_4-(CH_2)_3O$-{2,6-$(CH_2OH)_2$-4-$CH_3-C_6H_2$}].

Preparation of monomer 3

2,6-Bis(hydroxymethyl)-*p*-cresol (2.00 g) was transferred to a 250 ml Erlenmeyer flask, together with K_2CO_3 (5.00 g). The mixture was taken up in acetone (100 ml), and 1-bromobutane (1.3 ml) was added to the stirring dark orange–brown slurry. The mixture was refluxed under nitrogen for 3 days and then allowed to cool to room temperature. The solvent was removed using a rotary evaporator and the remaining residue extracted with CH_2Cl_2. This was filtered by gravity and the solvent was removed from the filtrate using a rotary evaporator to yield an orange oil. The oil was dissolved in a small amount of CH_2Cl_2 and hexane added to precipitate a white solid. This was purified by further washing with hexane to give a white solid in 18% yield.

^{1}H NMR (200 MHz, $CDCl_3$, δ): 0.99 (t, 2H, CH_3), 1.51 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.31 (s, 3H, CH_3), 3.86 (t, 2H, $-CH_2OAr$), 4.67 (s, 4H, $-CH_2OH$), 7.12 (s, 2H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 13.84 (CH_3), 19.18 (CH_2), 20.70 (CH_2), 32.41 ($Ar-CH_3$), 60.78 (CH_2OAr), 74.85 (CH_2OH), 129.19, 133.67, 133.96, 152.70 (Ar). M.p.: 62–63 °C.

Anal. Found: C, 69.87; H, 8.22. Calc. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%. Mass spectra (*m/z*): 224 [26%, molecular ion peak], 150 [100%, $C_9H_{10}O_2$], 91 [22%, C_7H_7], 65 [11%, C_5H_5].

Preparation of polymer (general procedure)

The organometallic bifunctional monomer was transferred to a nitrogen-purged Schlenk tube and dissolved in a minimum amount of dry toluene. Four equivalents of triethylamine were syringed into the stirred solution. An equivalent amount of terephthaloyl chloride was dissolved in dry toluene (8 ml) and this solution was added dropwise to the above mixture. Reactions were performed for either 2 or 24 h periods. During this time the reaction mixture was observed to turn cloudy. The mixture was then filtered by gravity into a round-bottomed flask containing hexane, when a solid product precipitated. The supernatant liquid was syringed off and the solid washed with hexane. The product was dried under vacuum. All other polyesters were prepared using a similar procedure.

4. Yield: 76%. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 1.40 (t, 2H, $FeCH_2$), 1.88 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 3.85 (t, 2H, CH_2OAr), 4.66 (s, 4H, CH_2OH), 4.69 (s, 5H, Cp), 5.44 (s, 4H, $PhCH_2OC(O)Ar$), 7.28 (s, 2H, Ar), 8.11–8.21 (m, 4H, Ar). IR (CH_2Cl_2), ν(CO) cm^{-1}: 2005 (s), 1943 (s), 1724 (m, acyl).

5. Yield: 73%. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 1.99 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.63 (t, 2H, $-CH_2$ Cp), 3.99 (t, 2H, $-CH_2Ar-$), 5.19–5.23 (m, 4H, Cp), 5.41 (s, 4H, $PhCH_2O$-C(O)Ar), 7.29 (s, 2H, Ar), 8.09–8.20 (m, 4H, Ar). IR (CH_2Cl_2), ν(CO) cm^{-1}: 2021 (s), 1925 (s), 1721 (m, acyl).

6. Yield: 82%. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 0.91 (m, 2H, CH_3), 1.38–1.50 (m, 2H, CH_2), 1.71–1.84 (m, 2H, CH_2), 2.33 (s, 3H, CH_3), 3.94 (t, 2H, $-CH_2OAr$), 5.43 (s, 4H, $PhCH_2O$-C(O)Ar), 7.28 (s, 2H, Ar), 8.15 (s, 4H,Ar). IR (KBr, DRIFTS), ν(CO) cm^{-1}: 1719 (m, acyl).

The structures of **4–6** are discussed below.

RESULTS AND DISCUSSION

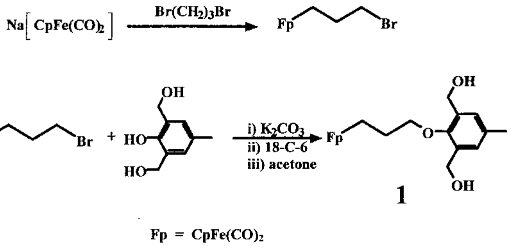
Monomer synthesis

Preparation

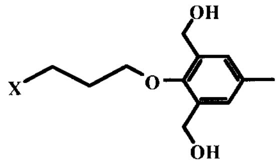
The organometallic monomers **1** and **2**, and the organic monomer **3** were synthesized using methods reported previously by Fréchet and co-workers.[22,23] Details of the synthetic routes for **1** and **2** are outlined in Schemes 1 and 2 respectively. We used 2,6-bis(hydroxymethyl)-*p*-cresol as the key reagent to incorporate a bifunctional moiety into our organometallic monomers. These methods entailed reacting a transition metal haloalkyl complex with 2,6-bis(hydroxymethyl)-*p*-cresol in the presence of K_2CO_3 and 18-crown-6. In this way, we have prepared both an M$-$C σ-bonded (**1**) and M$-$C π-bonded (**2**) organometallic monomer.

Monomer **1** represents the M$-$C σ-bonded compound in our studies. The synthesis of this compound (Scheme 1) was achieved by first preparing the precursor [(η^5-C_5H_5)$(CO)_2$-$Fe(CH_2)_3Br$].[24] This is then refluxed with 2,6-bis(hydroxymethyl)-*p*-cresol in acetone, in the presence of K_2CO_3 and 18-crown-6. Purification by column chromatography yielded a brown solid. This solid is stable in air, but decomposes in solution, in the absence of nitrogen.

The synthesis of monomer **2** followed a similar methodology to that of monomer **1**. Initially, the rhenium iodo-alkyl precursor was prepared, as per the literature procedure.[25] Starting from $CpRe(CO)_3$, the Cp ring is lithiated with *n*-BuLi at −78 °C and then 1,3-diidopropane added (Scheme 2). The iodopropyl complex was then reacted with 2,6-bis(hy-



Scheme 1.



X = CpFe(CO)$_2$ [1], (η^5-C$_5$H$_4$-R)Re(CO)$_3$ [2], CH$_3$ [3]

Figure 2. Structure of metal-containing diols.

droxymethyl)-*p*-cresol in acetone, in the presence of K_2CO_3 and 18-crown-6. This afforded monomer **2** as a stable, white solid in high yield (85%).

Our interest in forming polynuclear organometallic compounds by polycondensation reactions led us to study the effects of metal-containing moieties on polycondensation. Hence, it was decided to prepare the model organic monomer **3**. The reason for choosing this monomer was that the terminal $-CH_3$ group is isolobal with the organometallic moiety $[(\eta^5 - C_5H_5)Fe(CO)_2]$. Thus, the organometallic and organic structures of **1** and **3** respectively can be jointly considered under conditions for polycondensation. Monomer **3** was easily prepared, albeit in low yields, by reacting 1-bromobutane with 2,6-bis(hydroxymethyl)-*p*-cresol, in the presence of K_2CO_3 and 18-crown-6.

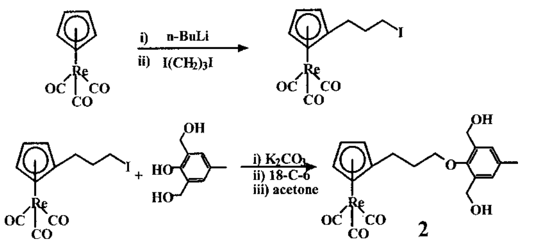
Characterization

The IR spectrum of the iron monomer **1** shows two strong v(CO) bands for the terminal carbonyl ligands at 2005 and 1945 cm^{-1}. These frequencies are similar to other CpFe(CO)$_2$R compounds and are in good agreement with the proposed structure. The rhenium complex **2** has two strong v(CO) bands, one a sharp peak at 2020 cm^{-1} and the other a broad one at 1923 cm^{-1}. These resemble carbonyl frequencies for compounds of the general formula $[(\eta^5\text{-}C_5H_4\text{-}R)Re(CO)_3]$.

The ^{1}H and ^{13}C NMR spectra for the monomers (**1**–**3**) exhibit similar resonances, characteristic of the bifunctional moiety (Fig. 2).

The peaks for the aliphatic $-CH_2-$ protons adjacent to the metal centre in monomer **1** is observed to be a triplet and is consistent with the proposed structure. The COSY spectrum shown in Fig. 3 clearly indicates their interaction. The COSY spectrum also confirms the broad band at 2.2 ppm to be the proton due to the hydroxyl group, and its coupling with the $-CH_2$ group next to the aromatic ring is clearly illustrated. Long-range coupling of this $-CH_2$ group and the methyl group with the aromatic protons is also clearly depicted.

The NMR spectrum of monomer **2** shows a similar spectrum to **1** except for the triplet due to the $-CH_2$ protons, which are now bonded to the Cp ring. These protons are now shifted greatly downfield, as a result of the overall deshielding effect of the CpRe(CO)$_3$ moiety. A splitting of the Cp signal is observed.



Scheme 2.

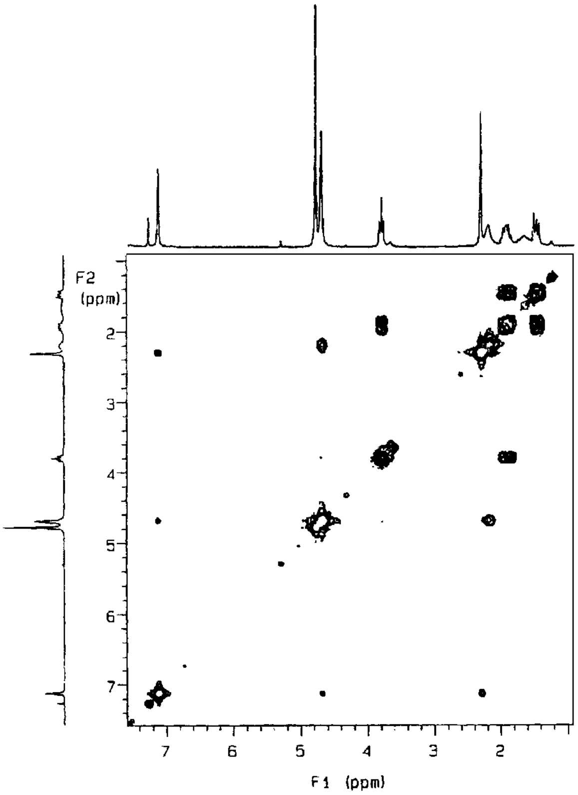


Figure 3. COSY NMR spectrum of monomer **1**.

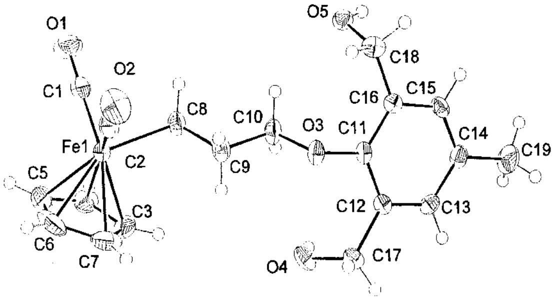


Figure 4. Molecular structure of monomer **1** showing the atom-numbering scheme.

Structural investigation

The characterization of compound **1** has been confirmed by X-ray single crystal structural analysis. The molecular structure with the atomic-numbering scheme is shown in Fig. 4. The crystallographic data are summarized in Table 1, and selected bond lengths and angles are given in Table 2.

Crystals of monomer **1** were grown by slow infusion of hexane into a dichloromethane solution of the monomer at −5 °C. The data were collected at low temperature. This new compound crystallizes in the orthorhombic unit cell, space group *Pbca*, with $Z = 8$, and adopts a slightly distorted tetrahedral geometry around the metal centre. The ORTEP plot of compound **1** in Fig. 4 clearly shows how the Cp ring is almost perpendicular to the plane of the aromatic ring. The Fe—CH_2 distance of 2.067(2) Å compares well with similar Fe—C (alkyl) single-bond lengths, which normally occur around 2.091 Å. There is a slight shortening of the bond length between C(9) and C(10). Known C^3_{sp}--C^3_{sp}bond lengths occur around 1.53 Å.

Polymer synthesis

Preparation

The organometallic polymers (**4**–**6**) shown in Scheme 3 were

Table 1. Crystallographic data and structure refinement for monomer **1**

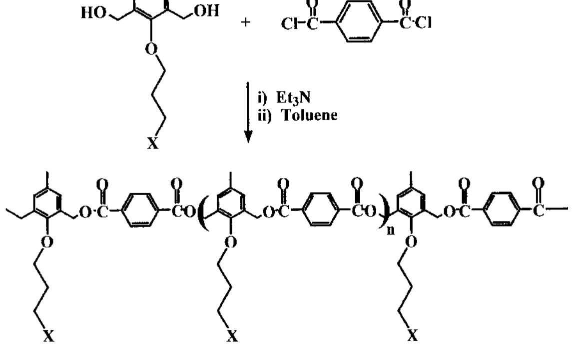
Empirical formula	$C_{19}H_{22}FeO_5$
Formula weight	386.22
Temperature (K)	173(2)
Wavelength (Å)	0.710 73
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	8.6803(3)
b (Å)	14.6794(3)
c (Å)	29.0830(10)
α (deg)	90
β (deg)	90
δ (deg)	90
Volume (Å^3)	3705.8(2)
Z	8
Density (calc.) (Mg^{1}m^{-3})	1.384
Absorption coefficient (mm^{-1})	0.839
F(000)	1616
Crystal size (mm^3)	0.67 × 0.50 × 0.33
θ range for data collection (deg)	2.81 to 25.34
Index ranges	$-9 \le h \le 10$, $-16 \le k \le 16$, $-33 \le l \le 13$
Reflections collected	7572
Independent reflections	3084 ($R_{\text{int}} = 0.0197$)
Completeness to $\theta = 25.34$ °(%)	90.9
Max. and min. transmission	0.7693 and 0.6034
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3084/0/260
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0327$, $wR_2 = 0.0712$
R indices (all data)	$R_1 = 0.0456$, $wR_2 = 0.0763$
Extinction coefficient	0.000 00(19)
Largest diff. peak and hole (e$^-$ Å^{-3})	0.250 and −0.253

Table 2. Selected bond lengths and angles for monomer **1**

Bond length	(Å)	Bond angle	(°)
Fe(1)–C(2)	1.743(3)	C(2)–Fe(1)–C(1)	93.67(12)
Fe(1)–C(1)	1.751(3)	C(2)–Fe(1)–C(8)	86.73(11)
Fe(1)–C(8)	2.067(2)	C(1)–Fe(1)–C(8)	87.05(10)
Fe(1)–C(4)	2.098(2)	O(2)–C(2)–Fe(1)	178.4(2)
Fe(1)–C(5)	2.099(2)	C(9)–C(8)–Fe(1)	115.78(15)
Fe(1)–C(6)	2.106(2)	O(1)–C(1)–Fe(1)	178.3(2)
Fe(1)–C(7)	2.109(2)		
Fe(1)–C(3)	2.113(2)		
O(1)–C(1)	1.151(3)		
O(2)–C(2)	1.152(3)		
C(4)–C(3)	1.392(3)		
C(4)–C(5)	1.403(4)		
C(8)–C(9)	1.519(3)		
C(9)–C(10)	1.503(3)		
C(3)–C(7)	1.393(4)		
C(5)–C(6)	1.391(4)		
C(7)–C(6)	1.425(4)		

prepared in high yields by reacting the organometallic monomers with terephthaloyl chloride in toluene solution. Triethylamine was added to remove HCl.

The newly formed metal-containing polyesters (**4** and **5**) both contain metal moieties in side chains pendant to the polymer backbone. The toluene-soluble fractions were dried under vacuum and all showed good solubilities in a range of common organic solvents. The toluene-insoluble fractions were also shown to be polymeric in nature, by comparison of the IR spectra of the toluene-soluble and toluene-insoluble fractions. The toluene-insoluble fraction is thought to be some higher molecular weight polyester.



X = CpFe(CO)$_2$ - [4], (η^5-C$_5$H$_4$-R)ReCO)$_3$ - [5], CH$_3$ - [6]

Scheme 3.

Polymer characterization

The ^{1}H NMR data for the new toluene-soluble polyesters are given in the Experimental section. Most of the peaks in the NMR spectra of the polymeric material resemble those of their respective precursors, with the exception of the peak due to the aliphatic protons adjacent to the hydroxy groups. For example, in monomer **1** this peak is found at 4.70 ppm, and was found to have shifted significantly to 5.44 ppm in compound **4**. This indicates that esterification has occurred at the aliphatic hydroxyl groups. However, for compound **4**, a peak is still observed at 4.70 ppm. This implies that the polymer chains have hydroxyl groups at their terminal endgroups, since all the starting organometallic monomer was consumed in the reaction. The same trends were observed in the ^{1}H NMR spectra of the polyesters formed from the rhenium monomer and the model organic monomer. Again, the aliphatic protons adjacent to the hydroxyl groups have shifted significantly downfield, confirming the formation of a polyester. For **5** and **6**, however, the small peak intensities for the aliphatic protons of the precursor, indicate that some of the chain ends in these compounds have hydroxy functionalities.

IR spectroscopy is also a useful diagnostic tool for confirming the formation of polyesters. The IR spectra for compounds **4** and **5** show strong, sharp absorption peaks at 2005 and 1943 cm^{-1}, and at 2021 and 1925 cm^{-1} respectively for the terminal carbonyl ligands. These absorptions are similar to those found in the monomeric precursors, and serve to confirm the integrity of the organometallic moieties in the polymer side-chains. The strong absorption band around 1720 cm^{-1} for all three compounds **4**, **5** and **6** is due to the acyl group found in the polyester backbone. These data serve to confirm the existence of the polyester linkage.

Molecular weight analysis

The average molecular weights of the polyesters were determined by GPC using THF as the eluent (Table 3). The molecular weights of the toluene-insoluble fractions could not be obtained as a result of their low solubilities, but these fractions were confirmed by IR spectroscopy to contain polyester linkages. The molecular weights of the toluene-soluble fractions show that the new compounds are oligomeric, low-molecular weight polyesters, which generally correspond to a degree of polymerization of about four. The presence of organometallic moieties in comparison with model compounds seems to indicate that the metal-containing moieties have a significant effect on the extent of polymerization. A study was conducted of the effect of time on the polymer yields. It was found that over a longer reaction period, the monomers bearing metal-containing moieties formed more toluene-insoluble fractions. These insoluble materials are also polymeric in nature, as was confirmed by comparison of its IR spectra with those of the toluene soluble fractions. Polymerizations carried out with

Table 3. GPC data for compounds **4, 5** and **6**

Compound	Polymerization reaction time (h)[a]	M_w[b]	M_n[c]	P.I.[d]
4	2	2724	1460	1.86
4	24	2482	1768	1.40
5	24	2612	1769	1.48
6	2	2327	1081	2.15
6	24	2604	1286	2.02

[a] The polymerization reactions were conducted in toluene.
[b] M_w = weight average molecular weight.
[c] M_n = number average molecular weight.
[d] P.I. = polydispersity index.

the purely organic monomer however gave largely soluble materials, which showed no significant decrease in yield irrespective of reaction time.

Thermal properties

The thermal behaviour of the organometallic polyesters was studied by DSC and TGA at a heating rate of 10.0 °Cmin^{-1}, under a nitrogen atmosphere. The organoiron compound **4** shows two exotherms, one small exotherm centred at 65 °C and a large, broad exotherm at 190 °C. The start of the broad endotherm corresponds with the onset of decomposition, without melting, which was observed using a Fischer–Johns hot-stage microscope, and found to be in the range 170–175 °C. A small endotherm was recorded at 75 °C. The TGA thermogram of **4** shows a two-step degradation, starting at 82 °C. The 8% weight loss observed to occur over the range 82 to 155 °C corresponds to the loss of the terminal carbonyl ligands of the iron-carbonyl moiety. This is followed by a mass loss to 250 °C associated with the decomposition of the complex.

The DSC trace for compound **5** shows two very small endothermic transitions, centred at 118 and 202 °C, and a small exothermic peak at 230 °C. The endothermic transition at 118 °C corresponds with the melting point of the solid at 115 °C, which was recorded on the Fischer–Johns hot-stage apparatus. This solid was observed to soften at around 78 °C. The TGA thermogram did not show an appreciable mass loss up to 250 °C. A weight loss of approximately 0.6% is observed from 59 to 116 °C, and cannot be attributed to any fragment.

These data seem to indicate that the rhenium compound is more thermally stable than the iron analogue, as it shows very little thermal activity up to 250 °C. This is generally the case for most rhenium compounds with alkyl groups bonded through the cyclopentadienyl ring. The organic polyesters also show very little thermal activity under similar conditions.

CONCLUSIONS

In this study, new polyesters were synthesized containing organometallic and alkyl pendant side chains. Three new bifunctional monomers were prepared and polymerized with terephthaloyl chloride in toluene solution, using triethylamine as a base. This gave low molecular weight, oligomeric materials, which were soluble in most organic solvents. Toluene-insoluble fractions were also isolated from the reaction mixture and their IR spectra were found to be identical to the toluene-soluble fractions. The former are thought to be higher molecular weight polymers. It can be seen that the presence of the metal moieties retards the extent of polymerization, compared with similar organic systems, and can be ascribed to the steric bulk of the metal centre and its ancillary ligands. The rhenium oligomers were found to more thermally stable than their iron analogues. The organometallic polyesters are currently being studied as potential catalysts in the Fischer–Tropsch process.

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